



## Effects of turbidity flows on organic matter accumulation, sulfate reduction, and methane generation in deep-sea sediments on the Iberia Abyssal Plain

PHILIP A. MEYERS<sup>1</sup>, JAMES E. SILLIMAN<sup>1</sup> and TIMOTHY J. SHAW<sup>2</sup>

<sup>1</sup>Marine Geology and Geochemistry Program, Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, U.S.A. and <sup>2</sup>Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, U.S.A.

**Abstract**—Non-steady-state sedimentation has affected preservation of organic matter in a Pliocene–Pleistocene turbidite sequence sampled by the Ocean Drilling Program at four closely spaced drill sites on the Iberia Abyssal Plain. Organic carbon concentrations average ca. 0.7% in sediments from Sites 897 and 898 and ca. 0.4% at Sites 899 and 900. Headspace concentrations of interstitial methane exceed 100,000 ppm in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, suggesting the presence of deep *in situ* methanogenic bacterial activity at Sites 897 and 898 and its absence at Sites 899 and 900. Two factors associated with the turbidity flows that created the sedimentary sequence evidently influenced post-depositional diagenesis at these sites. The principal factor is that the rapidly deposited turbidite sequences at Sites 897 and 898 protected organic matter from early oxic degradation and thereby permitted subsequent anoxic degradation to proceed. In contrast, organic matter in the more slowly deposited turbidites at Sites 899 and 900 was oxidized soon after deposition and was therefore not available for later microbial utilization. A lesser factor is that the turbidity flows may have obtained their entrained organic matter from different environments and consequently delivered organic matter with different characteristics. Both factors contributed to heterogeneity of the types and amounts of organic matter that accumulated in these deep-sea sediments, and this variability has influenced subsequent sulfate reduction and methanogenesis. Copyright © 1996 Elsevier Science Ltd

**Key words**—turbidites, Rock-Eval hydrogen indices, bulk  $\delta^{13}\text{C}$  values, C/N ratios, organic matter preservation, methanogenesis, interstitial sulfate, Iberia abyssal plain

### INTRODUCTION

Transfer and redeposition of organic matter from continental margins to deep-sea basins by turbidity flows are common. Turbidite emplacement is discontinuous, and it produces layers of sediment in which organic matter diagenesis is heterogeneous. Most models of organic matter degradation and related geochemical processes assume that steady-state reaction and diffusion are dominant, yet non-steady-state conditions prevail in many areas of sediment deposition. An example of non-steady-state deposition is those regions where deep-sea turbidites accumulate (Buckley and Cranston, 1988). Of particular importance, many petroleum source rocks accumulated in near-shore basins under similar conditions, and their compositions can reflect the episodic, non-uniform mode of turbidite deposition.

An opportunity to evaluate the consequences of turbiditic sediment accumulation on the initial preservation and subsequent bacterial utilization of organic matter over a time span of several million years is provided by the transect of sites drilled by Ocean Drilling Program (ODP) Leg 149 across the landward edge of the Iberia Abyssal Plain (Fig. 1).

Interstitial sulfate and methane concentrations are used as proxies of bacterially mediated anaerobic decomposition of organic matter within a sequence of turbidite layers that was emplaced during Pliocene–Pleistocene times.

### SEDIMENTARY SETTING

Seismic surveys performed in preparation for ODP Leg 149 identified a series of seaward-dipping reflectors on the landward edge of the Iberia Abyssal Plain (Sawyer *et al.*, 1994). A seismic profile spliced together from three east–west surveys suggested that the sediment layers represented by the reflectors were essentially continuous across the four proposed drill sites (Fig. 2). Water depths at these locations range from 5320 m at Site 897 to 5037 m at Site 900. Sediments obtained from the drilling transect revealed that the seismic reflectors consist of a succession of Neogene-to-Quaternary turbidite layers that vary somewhat in composition, but notably in thickness, among the four sites (Meyers and Shaw, 1996). Concentrations of  $\text{CaCO}_3$  vary between 80 and 0% in the turbidite sections from the four sites (Meyers and Silliman,

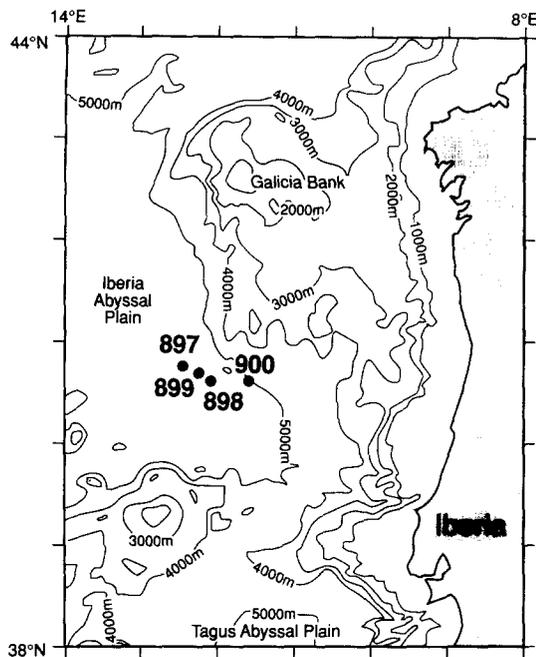


Fig. 1. Locations of ODP Sites 897, 898, 899, and 900 on the Iberia Abyssal Plain. Depth contours are given in meters.

1996). This variability reflects the intermix of pelagic and hemipelagic sediment types in these turbidites, which have contents ranging from nannofossil ooze to fine sand (Shipboard Scientific Party, 1994a, 1994b, 1994c, 1994d).

Sediments of the Pliocene–Pleistocene sections at Site 897 and 898 consist of interbedded distal turbidites that accumulated rapidly. Individual turbidite sequences range in thickness from 5 cm to over 1 m (Shipboard Scientific Party, 1994a, 1994b). The typical sequence consists of a layer of dark sand overlain by silty clays and capped by a thin layer of lightly colored nannofossil ooze. The dark color of the sands is attributed to higher organic carbon

contents in these layers. The small contribution of biogenic ooze indicates that pelagic sediments constitute a minor amount of the unit. Averaged sedimentation rates for these sections range from  $90 \text{ m my}^{-1}$  at Site 898 to  $532 \text{ m my}^{-1}$  at Site 897 (Shipboard Scientific Party, 1994a, 1994b). Although the averaged rates do not accurately represent the episodic nature of turbiditic sedimentation, they clearly show that Site 897 received thicker and more frequent turbiditic sediment emplacement than did Site 898, which is closer to Iberia (Fig. 1).

Drilling at Site 899 recovered sediments from the basal 50 m of a 132-m-thick Pliocene–Pleistocene layer of terrigenous distal turbidites. These turbidites are comparable in composition and texture to those at Sites 897 and 898, but they accumulated more slowly. Sedimentation rates are estimated to have averaged  $35 \text{ m my}^{-1}$  at Site 899 (Shipboard Scientific Party, 1994c). The Pliocene–Pleistocene sediments at Site 900 consist of siliciclastic muddy turbidites that accumulated even more slowly than at Sites 897 and 898. Individual turbidite sequences range in thickness between 10 cm to over 1 m and are separated by layers of nannofossil ooze up to 60 cm thick (Shipboard Scientific Party, 1994d). Averaged sedimentation rates at Site 900 range between 22 and  $24 \text{ m my}^{-1}$ .

The range of accumulation rates from  $532 \text{ m my}^{-1}$  to  $22 \text{ m my}^{-1}$  among the four sites may result from differences in sediment transport routes, but differences in bottom topography may also be important. The sites were positioned above basement highs to improve recovery of oceanic basement rock. The sedimentary units above the basement highs are typically thinner than in the surrounding basins because of sediment focusing into the topographic lows. Sites 897 and 898 were drilled prior to loss of the drill string, which subsequently limited drilling to the thinner sedimentary sequences present at Sites 899 and 900. The four Leg 149 sites consequently provide a unique comparison of dia-

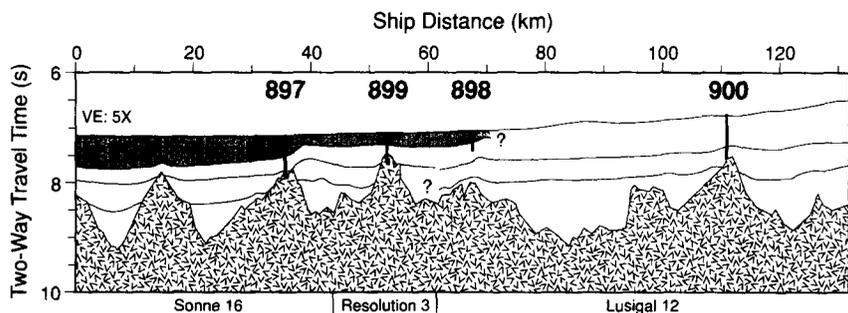


Fig. 2. A composite seismic profile of the sedimentary layers encountered by drilling during Leg 149. The Pliocene–Pleistocene turbiditic section that is the focus of this study is shown in stippling. The composite profile is spliced from seismic data generated by cruises of R/V Sonne, R/V Resolution, and R/V Lusigal. Vertical exaggeration (VE) is five-fold.

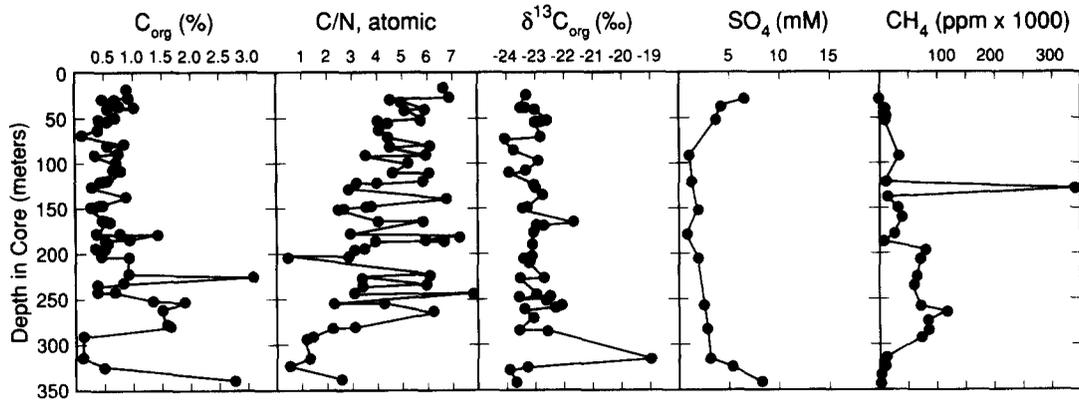


Fig. 3. Organic carbon concentrations, atomic organic C/total N ratios, organic  $\delta^{13}\text{C}$  values, dissolved interstitial sulfate concentrations, and headspace methane concentrations in Pliocene–Pleistocene sediments from ODP Site 897 on the Iberia Abyssal Plain. The base of the turbiditic section is 292 mbsf at this site.

genesis of sedimentary organic matter at closely spaced locations having different accumulation rates.

ment samples were used for Rock-Eval analyses and for headspace methane analyses.

ANALYSIS

The heterogeneous nature of the turbiditic sediments present at the four ODP sites makes it difficult to present a truly representative characterization of the amounts and types of organic matter contained in the Pliocene–Pleistocene sections. We have addressed this problem by analyzing the organic matter contents of samples collected at intervals that averaged 5 m at Sites 897, 898, and 899 and 10 m at Site 900, thereby obtaining averaged values from a large number of samples that span the variety of sediment types in the turbidite sections. Sediment samples were first freeze-dried and then treated with 3 N HCl to remove carbonates prior to subsequent analyses of organic carbon concentrations and isotopic contents. Whole-sedi-

Organic carbon concentrations

Amounts of residual organic carbon and nitrogen in carbonate-free sediment samples were measured with a Carlo Erba 1108 CHNS-O analyzer. This procedure involves heating the sample to 1020 °C and measuring the combustion products by gas chromatography (Verardo *et al.*, 1990). Known amounts of sulfanilamide are used to calibrate the instrument and to calculate the quantities of C and N released from the samples. Total organic carbon concentrations were then calculated on a whole-sediment basis, adjusting for carbonate concentrations determined by coulometric titration (Meyers and Silliman, 1996). C/N ratios were calculated on an atomic basis.

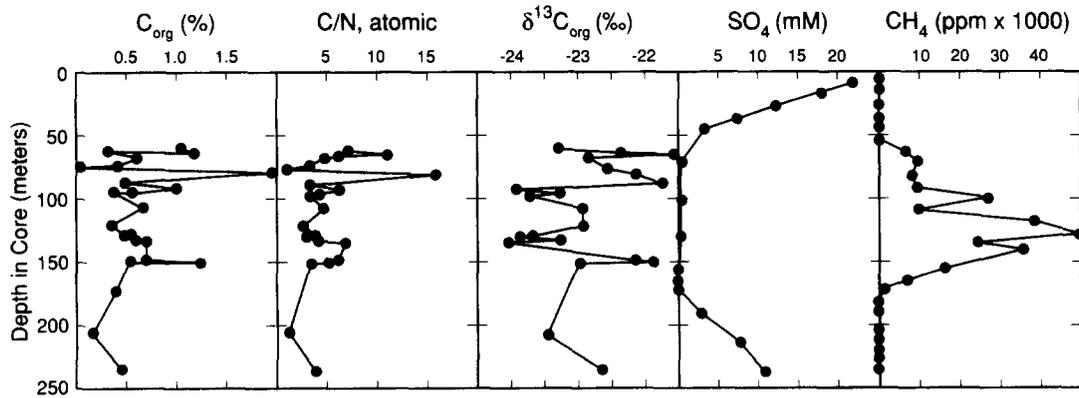


Fig. 4. Organic carbon concentrations, atomic organic C/total N ratios, organic  $\delta^{13}\text{C}$  values, dissolved interstitial sulfate concentrations, and headspace methane concentrations in Pliocene–Pleistocene sediments from ODP Site 898 on the Iberia Abyssal Plain. The base of the turbiditic section is 162 mbsf at this site.

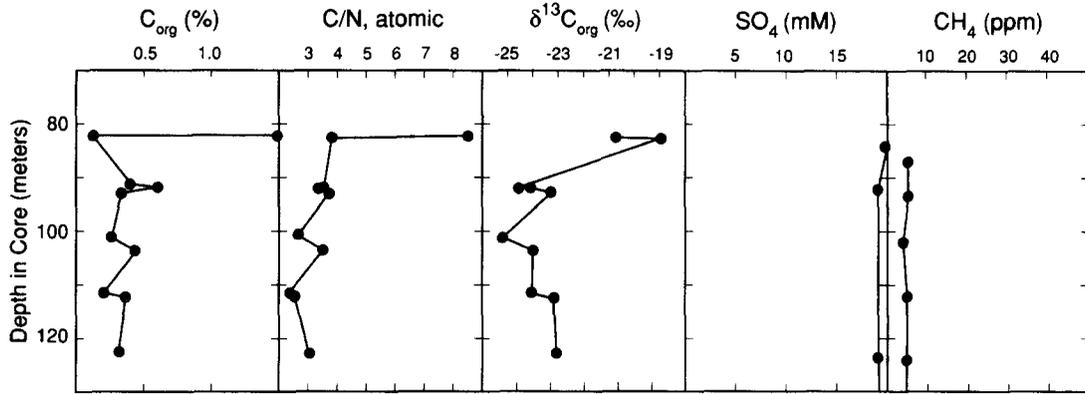


Fig. 5. Organic carbon concentrations, atomic organic C/total N ratios, organic  $\delta^{13}\text{C}$  values, dissolved interstitial sulfate concentrations, and headspace methane concentrations in Pliocene–Pleistocene sediments from ODP Site 899 on the Iberia Abyssal Plain. Coring commenced at 80 mbsf, and the base of the turbiditic section is 132 mbsf at this site.

#### Organic carbon isotope ratios

Organic carbon isotope measurements of Leg 149 samples were done in the Stable Isotope Laboratory at The University of Michigan. Organic carbon  $^{13}\text{C}/^{12}\text{C}$  ratios of the carbonate-free residues used for shorebased TOC analyses were measured after reacting the samples with CuO in evacuated and sealed quartz tubes for 3 hours at 800 °C. The  $\text{CO}_2$  produced by oxidation of the organic matter was analyzed with a Finnigan Delta S mass spectrometer. National Bureau of Standards carbon isotope standards were routinely used to calibrate the instruments. Results are reported relative to the PDB standard.

#### Rock-Eval pyrolysis

Rock-Eval analyses were done onboard the JOIDES Resolution using a Girdel II instrument. Rock-Eval pyrolysis of organic matter consists of heating samples to yield the amount of preformed

hydrocarbons volatile at 300 °C ( $S_1$ ), the amount of thermogenic hydrocarbons released between 300 °C and 600 °C ( $S_2$ ), and the amount of  $\text{CO}_2$  released during oxidic pyrolysis at 390 °C ( $S_3$ ). These values are combined with TOC values to calculate the hydrogen index ( $\text{HI} = 100 \times S_2/\text{TOC}$ , or mg hydrocarbons per g organic carbon) and the oxygen index ( $\text{OI} = 100 \times S_3/\text{TOC}$ , or mg  $\text{CO}_2$  per g organic carbon). The temperature of maximum hydrocarbon release during pyrolysis ( $T_{\text{max}}$ ) is also obtained and provides a measure of organic matter thermal maturity (Espitalié *et al.*, 1977).

#### Headspace methane concentrations

Samples for headspace gas analyses were routinely taken from each 9 m core immediately after arrival on deck. A 5 cm<sup>3</sup> plug of core was removed from the end of a freshly cut core section and placed in a glass vial that was then sealed with a rubber septum and a metal crimp. Septum-sealed glass vials were heated at 70 °C for 30 min.

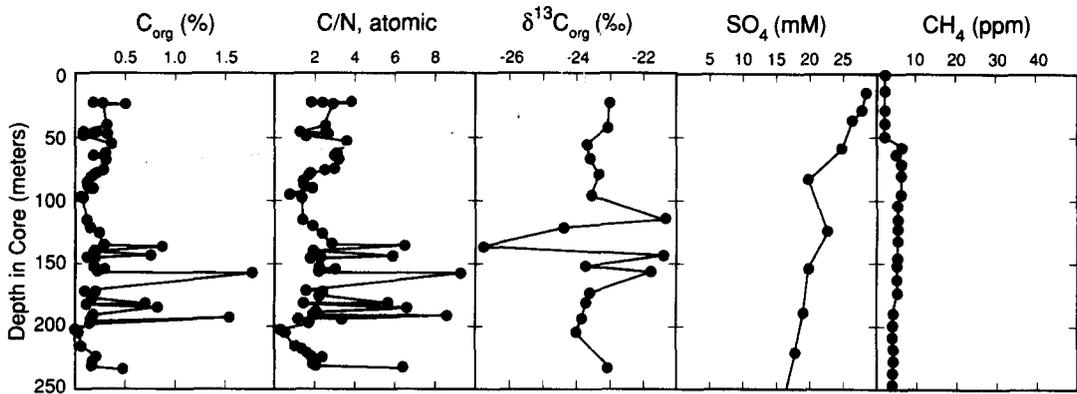


Fig. 6. Organic carbon concentrations, atomic organic C/total N ratios, organic  $\delta^{13}\text{C}$  values, dissolved interstitial sulfate concentrations, and headspace methane concentrations in Pliocene–Pleistocene sediments from ODP Site 900 on the Iberia Abyssal Plain. The base of the turbiditic section is 67 mbsf at this site.

Headspace gases were drawn into a syringe and injected into a Carle AGC 1000/Model 211 gas chromatograph equipped with a flame ionization detector.

## RESULTS AND DISCUSSION

Individual samples from the mix of sediment lithologies that constitute the Pliocene–Pleistocene turbidite layers predictably have a range of organic matter contents. We have consequently averaged bulk organic matter data from each site to allow comparisons of the amounts and types of material present in the Pliocene–Pleistocene sedimentary units at the four sites. We have not, however, averaged the contents of interstitial water samples, because these relatively mobile constituents are probably fairly representative of the 9 m core intervals at which they were collected.

### *Organic carbon concentrations*

Averaged organic carbon concentrations in the turbidite sections are: Site 897, 0.78%; Site 898, 0.68%; Site 899, 0.44%; Site 900, 0.36%. These values are slightly higher than the average organic carbon content of 0.2% of deep-sea sediments and rocks from DSDP Legs 1 through 33 compiled by McIver (1975). Many of the individual samples, however, are very low in organic carbon (Figs 3–6). Of particular note, the uppermost section that was drilled at Sites 897, 898, and 899 seems to be the same continuous series of turbidites (Fig. 2), yet the TOC concentrations at Sites 897 and 898 are significantly higher than those at Site 899, which is located between the other two. In addition, TOC concentrations are variable with depth in this uppermost section as it is expressed at each of the four drill sites. The delivery of organic matter to the landward edge of the Iberia Abyssal Plain has evidently varied both spatially and temporally during the Pliocene and Pleistocene. Part of this variability may result from the turbidites originating from different locations on the Iberia Margin, but the primary cause of the differences in concentrations is probably the greater thicknesses of the turbidites at Sites 897 and 898 relative to Sites 899 and 900, which affects the degree of post-depositional preservation of organic matter (Shaw and Meyers, 1996; Meyers and Shaw, 1996).

The differences in organic carbon concentration suggest that a greater fraction of the available carbon was consumed after burial at Sites 899 and 900, where accumulation rates are low, than at Sites 897 and 898, where rates are high. Although concentrations are variable at each site, averaged concentrations are lower at Sites 899 and 900 than at Sites 897 and 898. This difference is consistent with more efficient and therefore more complete consumption of organic carbon under oxic interstitial water con-

ditions as opposed to anoxic sedimentary conditions. Preservation of organic carbon is consequently poorer in the more slowly accumulated sediments at Sites 899 and 900.

### *Organic matter C/N ratios*

Atomic C/N ratios help to distinguish between algal and land-plant origins of sedimentary organic matter. Algae typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of 20 and greater (Premuzic *et al.*, 1982; Jasper and Gagosian, 1990; Meyers, 1994; Prahl *et al.*, 1994). This distinction arises from the absence of cellulose in algae and its abundance in vascular plants. Algae are therefore relatively rich in nitrogenous protein material compared to land plants, and this difference in elemental compositions is largely preserved in sedimentary organic matter.

The averaged atomic C/N ratios from the four locations are: Site 897,  $4.6 \pm 1.6$ ; Site 898,  $3.8 \pm 3.9$ ; Site 899,  $3.7 \pm 1.8$ ; Site 900,  $2.9 \pm 2.1$  (Meyers and Silliman, 1996). These relatively low ratios indicate that marine contributions dominate the organic matter compositions in these turbidite layers and that the organic matter has been at least partially degraded within its host sediment. Degradation of organic matter in marine sediments tends to lower C/N ratios as nitrogenous compounds break down to produce ammonia, which is retained by clay minerals (Müller, 1977), and the CO<sub>2</sub> released by oxidation of organic carbon diffuses away. Some of the samples have C/N ratios of 1 or 2; these are too low to represent undegraded algal organic matter. A few samples from Site 898 have C/N ratios between 10 and 20 (Fig. 4). These samples may contain elevated proportions of land-derived organic matter. Alternatively, they may contain marine organic matter in which partial degradation selectively removed nitrogenous material prior to sedimentation and that was subsequently preserved well. The higher average C/N ratio of 4.6 in the Site 897 sediments, which is close to that of fresh algal matter, suggests that the marine organic matter at this location has experienced less degradation than at the other sites. The differences in C/N ratios from site to site and with depth at each site suggests spatial and temporal variations in the degree of preservation of marine-derived organic matter in these turbidites.

### *Organic carbon isotope ratios*

Organic carbon isotopic ratios are useful to distinguish between marine and continental plant sources of sedimentary organic matter. Most photosynthetic plants incorporate carbon into organic matter using the C<sub>3</sub> Calvin pathway which biochemically discriminates against <sup>13</sup>C to produce a δ<sup>13</sup>C shift of about –20‰ from the isotope ratio of the inorganic carbon source. Organic matter produced from atmospheric CO<sub>2</sub> (δ<sup>13</sup>C ≈ –7‰) by

land plants using the C<sub>3</sub> pathway consequently has an average  $\delta^{13}\text{C}$  (PDB) value of ca.  $-27\%$  (O'Leary, 1988). The source of inorganic carbon for marine algae is dissolved bicarbonate, which has a  $\delta^{13}\text{C}$  value of ca.  $0\%$ . Marine organic matter consequently typically has  $\delta^{13}\text{C}$  values between  $-20$  and  $-22\%$ . The  $\approx 7\%$  difference between organic matter produced by C<sub>3</sub> land plants and marine algae has been used to trace the delivery and distribution of organic matter to sediments of ocean margins (Newman *et al.*, 1973; Prahl *et al.*, 1994). Carbon isotope ratios can be affected, however, by photosynthetic dynamics and by post-depositional diagenesis (Dean *et al.*, 1986; McArthur *et al.*, 1992) and consequently must be interpreted cautiously. Prominent among these are the availability of CO<sub>2</sub> during photosynthesis and the possibility of selective diagenesis of organic matter fractions that are isotopically heavy or light. Any diagenetic isotope shift appears to be small, less than  $2\%$  (Hayes *et al.*, 1989; McArthur *et al.*, 1992; Fontugne and Calvert, 1992; Meyers, 1994). Increased availability of dissolved CO<sub>2</sub> to algae, however, would enhance their isotopic discrimination and produce marine organic matter that is isotopically light (Hayes *et al.*, 1989), as would increased delivery of isotopically light fluvial dissolved inorganic carbon (Fontugne and Calvert, 1992) from areas on the continental shelf where some of the turbidite-borne organic matter may have originated.

Organic  $\delta^{13}\text{C}$  values of sediment samples from the four sites average ca.  $-23\%$ , which indicates that most of the organic matter originated from marine production (Meyers, 1994). The range of these values, from  $-19.0\%$  to  $-26.8\%$  (Figs 3–6), suggests, moreover, that the origins have not been identical in all the turbidite layers. For example, the isotopically heavy organic matter may have been produced by marine algae during times of diminished availability of dissolved CO<sub>2</sub>, such as those that accompany spring blooms or periods of upwelling. The organic matter in the isotopically heavy samples may have therefore originated from coastal areas of high productivity 200 km to the east of the Abyssal Plain and record transport of continental shelf sediment to the deep-sea by turbidity flows. The isotopically light organic matter, in contrast, may contain a substantial fraction of continental material, again evidence of the importance of turbidity-flow delivery of material to these locations.

#### *Interstitial sulfate concentrations*

Concentrations of pore water sulfate reported by Shaw and Meyers (1996) decrease nearly to zero in the upper 50 m of sediment at Sites 897 and 898 and remain near zero at the base of the turbidite unit at both sites (Figs 3 and 4). The decrease indicates an active zone of sulfate reduction at both sites. Below the turbidite section (292 mbsf at Site

897; 162 mbsf at Site 898), sulfate concentrations recover to 15–18 mM. Sulfate reduction appears not to occur in these deeper sediments. In terms of redox conditions, most of the turbidite unit present at Sites 897 and 898 is an anoxic section bounded by an upper and a lower sulfate reservoir.

Concentrations of pore water sulfate in sediments of Sites 899 and 900 contrast to the pattern present in Sites 897 and 898 by progressively decreasing from near-seawater values ( $\approx 29$  mM) as sediment depth increases, but never reaching zero (Figs 5 and 6). At least 15 mM interstitial sulfate is present in all parts of the turbidite section as expressed at these two sites.

The activity of sulfate-reducing bacteria is generally limited by the availability of low-molecular-weight organic compounds. As a result, organic matter degradation via sulfate reduction must be preceded by an intermediate fermentation that can break down organic compounds into smaller molecules. Organic matter at Sites 897 and 898 has slightly higher C/N ratios than the organic matter at Sites 899 and 900 (Figs 3–6), which could be an indicator of better preservation of organic matter in these sediments. The high accumulation rates at Sites 897 and 898 evidently impacted subsequent microbial activity.

#### *Headspace methane concentrations*

Concentrations of headspace methane are high in the Pliocene–Pleistocene turbidite sections at Sites 897 and 898 and drop to near-background levels in underlying sediments (Figs 3 and 4). Two sources of the dissolved gas are possible. First, methane-rich gases from some deeper origin may have diffused into the sections, which consist of turbiditic sand, silt, and clay layers. The locations of Sites 897 and 898 on basement highs make this an especially reasonable possibility. Evidence for diffusional migration of methane into porous sediments from deeper sources has been found at Sites 762 and 763 on the Exmouth Plateau, where a known thermogenic source exists in underlying Jurassic rocks (Snowdon and Meyers, 1992). However, a similar deep source for the methane on the Iberia Abyssal Plain is presently unknown. A second, more likely possibility is *in situ* formation by methanogenic bacteria. High C<sub>1</sub>/C<sub>2</sub> ratios and the absence of higher-molecular-weight hydrocarbon gases indicate that the gas is biogenic, as opposed to thermogenic, in origin (Shipboard Scientific Party, 1994a, 1994b). The source of the methane is probably from *in situ* microbial fermentation of the marine organic matter present in this turbiditic sequence. Similar microbial production of methane from marine organic matter has been inferred from high biogenic gas concentrations in Pliocene–Pleistocene sediments from Site 532 on the Walvis Ridge (Meyers and Brassell,

1985) and in Middle Miocene sediments from Site 767 in the Celebes Sea (Rangin *et al.*, 1990).

Headspace methane concentrations are low in sediments below the Pliocene–Pleistocene turbidite layers at Sites 897 and 898 (Figs 3 and 4). Sub-bottom depths of 200–300 m are not likely to be important in limiting microbial methane production inasmuch as viable heterotrophic bacteria have been isolated from Upper Miocene sediments over 500 mbsf at Site 798 in the Japan Sea (Cragg *et al.*, 1992). Algal organic matter is generally more reactive and therefore more suitable for microbial utilization than is detrital or continental organic matter (Lallier-Vergès *et al.*, 1993). The lower amounts of metabolizable organic matter in deeper sediments is probably the major factor in precluding methanogenesis. The reappearance of significant concentrations of interstitial sulfate, an electron acceptor that enables organic matter oxidation, below the Pliocene–Pleistocene turbidite sequences (Figs 3 and 4) indicates that methanogenesis is not energetically favored in the deeper sediments (Claypool and Kvenvolden, 1983).

In contrast to Sites 897 and 898, the sediments of Sites 899 and 900 contain essentially no methane (Figs 5 and 6). Because methane is present at sub-bottom depths at Sites 897 and 898 that are similar to those at Sites 899 and 900, diffusion out of the sediments is unlikely to be important. Instead, it is probable that methane was never generated in the sediments at Sites 899 and 900. Organic carbon concentrations are on average lower at these two sites than at Sites 897 and 898, and the organic matter that is present in the sediments appears to be detrital and of low metabolizable value (Fig. 7; Meyers and Silliman, 1996). The consequent absence of suitable substrate for microbial activity probably prevented methanogenesis. Moreover, interstitial sulfate is present at near-seawater concentrations in the sediments of Sites 899 and 900 (Figs 5 and 6), and the presence of this terminal electron acceptor is a further constraint on methanogenic bacterial activity (Claypool and Kvenvolden, 1983). Alternatively, the presence of significant amounts of dissolved sulfate may reflect the absence of any significant microbial activity in the sediments at Sites 899 and 900.

#### Rock-Eval analyses

Rock-Eval pyrolysis was originally developed to characterize the organic matter present in oil source rocks (Espitalié *et al.*, 1977), which typically is more thermally mature and at higher concentrations than is the organic matter commonly found in sediments obtained by scientific ocean drilling. Rock-Eval analyses of immature deep-sea sediments have nonetheless proved valuable in helping to distinguish between continental and marine origins of organic matter in such samples. Land-plant organic matter

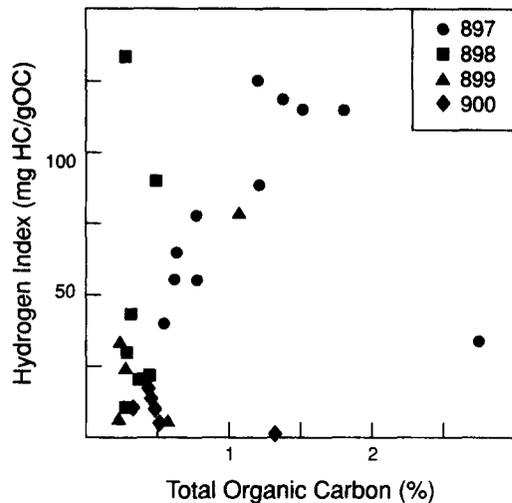


Fig. 7. Rock-Eval hydrogen index values and total organic carbon concentrations for sediments from ODP Sites 897, 898, 899, and 900 on the Iberia Abyssal Plain. Low values for both parameters suggests that the organic matter in sediments from all four sites has been oxidized from its initial marine (Type II) character.

is usually rich in woody components and consequently has lower HI values and higher OI values than those found in lipid-rich and cellulose-poor algal organic matter. This distinction between organic matter from continental and marine sources becomes blurred, however, by diagenesis as marine matter oxidizes and gradually takes on HI and OI values similar to those of land-plant material.

A Van Krevelen-type plot of the HI and OI values (Fig. 7) suggests that the Leg 149 turbiditic sediments contain Type III (land-derived) organic matter (Meyers and Silliman, 1996). This source assignment for the organic matter conflicts, however, with the low C/N ratios and the high  $\delta^{13}\text{C}$  values for these samples, which suggest that the organic matter is predominantly marine. The contradiction between the Rock-Eval source characterization and the elemental and isotopic source characterizations indicates that the original Type II (marine) organic matter has been heavily oxidized, probably by microbial reworking. The microbial reworking of the organic matter in the turbiditic units at Sites 899 and 900 evidently happened prior to, or shortly after, redeposition of these sediments on the Iberia Abyssal Plain, inasmuch as little sulfate reduction has occurred at these locations (Figs 5 and 6). In contrast, *in situ* microbial reprocessing of organic matter deeper below the sediment/water interface is indicated at Sites 897 and 898 by the disappearance of interstitial sulfate and accompanying appearance of pore-water methane with increasing sediment depth at these locations (Figs 3 and 4). The HI values of samples from Sites 897 and 898 are in general higher than those of samples from

Sites 899 and 900 (Fig. 7), indicating that some of the marine organic matter at Sites 897 and 898 has not been as extensively microbially reworked as at Sites 899 and 900. The range of HI values present in sediments from Sites 897 and 898 indicates, moreover, that the amount of microbial reworking has been variable at these sites, which is consistent with non-steady-state turbiditic sedimentation on the landward edge of the Iberia Abyssal Plain.

#### *Organic matter oxidation*

The ratio of carbon degraded under oxic versus anoxic conditions will impact the character of the surviving buried carbon. In the more rapidly accumulated turbidites of Sites 897 and 898, much of the carbon degradation occurred under anoxic conditions (Shaw and Meyers, 1996). At depths greater than 10 cm into any one turbidite sequence, the maximum oxygen flux into the remaining interval can be calculated to be on the order of  $0.02 \text{ moles m}^{-2} \text{ yr}^{-1}$ , assuming a bottom water oxygen concentration of  $200 \mu\text{M}$ . For thick turbidite sequences such as those in Sites 897 and 898, sulfate reduction was consequently the predominant mode of carbon degradation. The character of the surviving carbon in deep-sea turbidite sequences in general may therefore be a function of the rate of burial, resulting in diagenetic differences from location to location and from depth to depth.

The turbidite layers in the sequences at Sites 899 and 900 are thinner and were deposited less frequently than at Sites 897 and 898. The generally thicker intervals of interlayered nannofossil ooze suggest longer periods of slow sedimentation. In thin turbidite sequences, oxic degradation of the carbon probably occurred via the 'burn down' mechanism described by Thomson *et al.* (1984, 1993), Wilson *et al.* (1986) and Pruyers *et al.* (1993). Oxygen would slowly diffuse into the carbon-enriched turbidite layer during the slow deposition of the pelagic oozes that separate turbidite layers at these two sites. The slow sedimentation and thin turbidite emplacement would result in early diagenetic oxic degradation being the predominant mode of organic carbon degradation, and little oxidizable, or microbially metabolizable, organic matter would survive in deeper sediments. Sulfate reduction and subsequent methane production deeper in the sediments would therefore not be significant.

If the origins of the turbidite layers on the Iberia Abyssal Plain are assumed to be similar settings on the Iberia Margin, then the turbidite sequences encountered at the four drill sites approximate compositionally uniform deposits that originally differed only in their thickness. Subsequent oxidation of organic matter, however, would proceed by different geochemical processes depending on the thickness of each layer. The thinner deposits would have a

greater proportion of organic carbon oxidized under oxic conditions, whereas sub-bottom anoxic conditions would lead to sulfate reduction and eventually methanogenesis in the thicker deposits. Interstitial sulfate concentrations support this concept (Shaw and Meyers, 1996). The presence of relatively high sulfate concentrations in sediments from Sites 899 and 900 indicates that little reactive organic carbon survived oxic degradation in these slowly accumulated turbidites to be available to consume sulfate. In contrast, sulfate consumption during organic matter oxidation has removed essentially all of the dissolved sulfate from the sediments of Sites 897 and 898, and these sediments are rich in interstitial methane.

Sediments in the Pliocene–Pleistocene turbidite sequences sampled at Sites 897, 898, 899 and 900 illustrate the interplay of sedimentation rates and non-steady-state diagenesis and oxidation of organic matter in deep-sea sediments. Partially preserved algal organic matter is generally more reactive and therefore more suitable for microbial utilization than is detrital or continental organic matter (Lallier-Vergès *et al.*, 1993), and the availability of metabolizable organic matter has evidently impacted microbial processes in these sediments. Sulfate reduction proceeds with depth at Sites 897 and 898 where adequate amounts of reactive organic matter remain available to support bacterial activity. In contrast, little sulfate reduction occurs at Sites 899 and 900. Headspace concentrations of interstitial methane are high in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Because methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, the existence of *in situ* methanogenic bacterial activity evidently occurs at sub-bottom depths of several hundred meters at Sites 897 and 898 (Claypool and Kvenvolden, 1983). Similar methanogenic activity appears to be absent at Sites 899 and 900. Heterogeneity in turbiditic sediment delivery and consequent burial and preservation of organic matter has controlled sulfate reduction and methanogenesis in these deep-sea sediments.

#### SUMMARY AND CONCLUSIONS

The amounts and types of organic matter and concentrations of dissolved sulfate and headspace methane have been determined in sediments of a Pliocene–Pleistocene distal turbidite sequence that was recovered during Leg 149 in four closely spaced drill sites on the landward edge of the Iberia Abyssal Plain (Sawyer *et al.*, 1994). Organic carbon concentrations average 0.7% in this sequence at Sites 897 and 898 and 0.4% at Sites 899 and 900. Atomic C/N ratios are generally between 3 and 10 and indicate an algal origin (Meyers, 1994). Organic  $\delta^{13}\text{C}$  values vary little from  $-23\%$ , which is typical

of marine algae (Meyers, 1994). Rock-Eval results reveal that the marine organic matter in the sediments is heavily oxidized. Headspace concentrations of interstitial methane exceed 100000 ppm in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Partially preserved marine organic matter is present in the sediments of Sites 897 and 898, whereas poorly preserved, detrital marine material is found at the other two sites. Moreover, the degree of preservation of organic matter in Site 897 and 898 sediments fluctuates with depth. A correlation between low organic matter C/N ratios and low concentrations of organic carbon indicates that post-depositional diagenesis of organic matter controls TOC concentrations. The amount of *in situ* oxidation of organic matter has been controlled by rates of turbidite sedimentation, which are high at Sites 897 and 898 and low at Sites 899 and 900. An additional factor is that the turbidity flows may have obtained their entrained organic matter from different environments and consequently delivered organic matter with different characteristics. Both factors contribute to heterogeneity of the types and amounts of organic matter in these deep-sea sediments, and this variability has influenced subsequent sulfate reduction and methanogenesis. Methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, suggesting the presence of deep *in situ* methanogenic bacterial activity at Sites 897 and 898 and its absence at Sites 899 and 900.

*Acknowledgements*—We appreciate the thoughtful suggestions provided by W. E. Dean and D. R. Oros to improve our paper. P.A.M. and T.J.S. thank the Ocean Drilling Program, funded by the National Science Foundation and IPOD countries, for providing them with the special opportunity to spend two, curiously enjoyable months at sea. Dale Austin rendered our crude drawings into intelligible illustrations. Post-cruise studies were supported by grants from JOI-USSSP.

#### REFERENCES

- Buckley D. E. and Cranston R. E. (1988) Early diagenesis in deep sea turbidites: the imprint of paleo-oxidation zones. *Geochim. Cosmochim. Acta* **52**, 2925–2939.
- Claypool G. E. and Kvenvolden K. A. (1983) Methane and other hydrocarbon gases in marine sediment. *Ann. Rev. Earth Planet. Sci.* **11**, 299–327.
- Cragg B. A., Harvey S. M., Fry J. A., Herbert R. A. and Parkes R. J. (1992) Bacterial biomass and activity in the deep sediment layers of the Japan Sea, Hole 798B. In *Proc. ODP, Sci. Results* (Edited by Pisciotto K. A., Ingle J. C., Jr, von Breyman M. T., Barron J., *et al.*), Vol. 127/128, Pt. 1. pp. 761–776. College Station TX (Ocean Drilling Program).
- Dean W. E., Arthur M. A. and Claypool G. E. (1986) Depletion of  $^{13}\text{C}$  in Cretaceous marine organic matter: source, diagenetic, or environmental signal?. *Mar. Geol.* **70**, 119–157.
- Espitalié J., Laporte J. L., Madec M., Marquis F., Leplat P., Paulet J. and Boutefeu A. (1977) Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Français Pétrole* **32**, 23–42.
- Fontugne M. R. and Calvert S. E. (1992) Late Pleistocene variability of the carbon isotopic composition of organic matter in the eastern Mediterranean: monitor of changes in carbon sources and atmospheric  $\text{CO}_2$  levels. *Paleoceanogr.* **7**, 1–20.
- Hayes J. M., Popp B. N., Takigiku R. and Johnson M. W. (1989) An isotopic study of biogeochemical relationships between carbonates and organic carbon in the Greenhorn Formation. *Geochim. Cosmochim. Acta* **53**, 2961–2972.
- Jasper J. P. and Gagosian R. B. (1990) The sources and deposition of organic matter in the Late Quaternary Pygmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* **54**, 1117–1132.
- Lallier-Vergès E., Bertrand P. and Desprairies A. (1993) Organic matter composition and sulfate reduction intensity in Oman Margin sediments. *Mar. Geol.* **112**, 57–69.
- McArthur J. M., Tyson R. V., Thomson J. and Matthey D. (1992) Early diagenesis of marine organic matter: alteration of the carbon isotopic composition. *Mar. Geol.* **105**, 51–61.
- McIver R. (1975) Hydrocarbon occurrences from JOIDES Deep Sea Drilling Project. *9th Proc. World Pet. Congr.* **2**, 269–280.
- Meyers P. A. (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* **144**, 289–302.
- Meyers P. A. and Brassell S. C. (1985) Biogenic gases in sediments deposited since Miocene times on the Walvis Ridge, South Atlantic Ocean. In *Planetary Ecology* (Edited by Caldwell D. E., Brierly J. A. and Caldwell C. L.), pp. 69–80. Wiley, New York.
- Meyers P. A. and Shaw T. J. (1996) Organic matter, sulfate reduction, and methanogenesis in Pliocene–Pleistocene turbidites at ODP Sites 897, 898, 899, and 900, Iberia Abyssal Plain. In *Proc. ODP, Sci. Results* (Edited by Whitmarsh R. B., Sawyer D. S., Klaus A. *et al.*), Vol. 149, pp. 705–712. Ocean Drilling Program, College Station TX.
- Meyers P. A. and Silliman J. E. (1996) Organic matter in Pleistocene to Pliocene turbidites from Sites 897, 898, 899, and 900, Iberia Abyssal Plain. In *Proc. ODP, Sci. Results* (Edited by Whitmarsh R. B., Sawyer D. S., Klaus A. *et al.*), Vol. 149, pp. 305–313. Ocean Drilling Program, College Station TX.
- Müller P. J. (1977) C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **41**, 765–776.
- Newman J. W., Parker P. L. and Behrens E. W. (1973) Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico. *Geochim. Cosmochim. Acta* **37**, 225–238.
- O'Leary M. H. (1988) Carbon isotopes in photosynthesis. *Bioscience* **38**, 328–336.
- Prahl F. G., Ertel J. R., Goni M. A., Sparrow M. A. and Eversmeyer B. (1994) Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochim. Cosmochim. Acta* **58**, 3055–3048.
- Premuzic E. T., Benkovitz C. M., Gaffney J. S. and Walsh J. J. (1982) The nature and distribution of organic matter in the surface sediments of world oceans and seas. *Org. Geochem.* **4**, 63–77.
- Pruyvers P. A., de Lange G. J., Middelburg J. J. and Hydes D. J. (1993) The diagenetic formation of metal-rich layers in sapropel-containing sediments in the east-

- ern Mediterranean. *Geochim. Cosmochim. Acta* **57**, 527–536.
- Rangin C., Silver E., von Breymann M. T. *et al.* (1990) Site 767. In *Proc. ODP, Init. Repts* (Edited by Rangin C., Silver E. *et al.*), Vol. 124, pp. 121–193. Ocean Drilling Program, College Station, TX.
- Sawyer D. S., Whitmarsh R. B., Klaus A. *et al.* (1994) *Proc. ODP, Init. Repts.* 149. Ocean Drilling Program, College Station TX.
- Shaw T. J. and Meyers P. A. (1996) The implications of turbidite-driven changes in sediments of the Iberia Abyssal Plain. In *Proc. ODP, Sci. Results* (Edited by Whitmarsh R. B., Sawyer D. S., Klaus A. *et al.*), Vol. 149, pp. 301–304. Ocean Drilling Program, College Station TX.
- Shipboard Scientific Party (1994a) Site 897. In *Proc. ODP, Init. Repts* (Edited by Sawyer D. S., Whitmarsh R. B., Klaus A. *et al.*), Vol. 149, pp. 41–113. Ocean Drilling Program, College Station, TX.
- Shipboard Scientific Party (1994b) Site 898. In *Proc. ODP, Init. Repts.* *et al.*), Vol. 149, pp. 115–146. Ocean Drilling Program, College Station, TX.
- Shipboard Scientific Party (1994c) Site 899. In *Proc. ODP, Init. Repts.* (Edited by Sawyer D. S., Whitmarsh R. B., Klaus A. *et al.*), Vol. 149, pp. 147–209. Ocean Drilling Program, College Station, TX.
- Shipboard Scientific Party (1994d) Site 900. In *Proc. ODP, Init. Repts.* *et al.*), Vol. 149, pp. 211–262. Ocean Drilling Program, College Station, TX.
- Snowdon L. R. and Meyers P. A. (1992) Source and maturity of organic matter in sediments and rocks from Sites 759, 760, 761, and 764 (Wombat Plateau) and Sites 762 and 763 (Exmouth Plateau). In *Proc. ODP Sci. Results* (Edited by von Rad U., Haq B. U. *et al.*), Vol. 122, pp. 309–315. Ocean Drilling Program, College Station, TX.
- Thomson J., Higgs N. C., Croudace I. W., Colley S. and Hydes D. J. (1993) Redox zonation of elements at an oxic/post-oxic boundary in deep-sea sediments. *Geochim. Cosmochim. Acta* **57**, 579–595.
- Thomson J., Wilson T. R. S., Culkin F. and Hydes D. J. (1984) Non-steady state diagenetic record in eastern equatorial Atlantic sediments. *Earth Planet. Sci. Lett.* **71**, 23–30.
- Verardo D. J., Froelich P. N. and McIntyre A. (1990) Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA01500 analyzer. *Deep-Sea Res.* **37**, 157–165.
- Wilson T. R. S., Thomson J., Hydes D. J., Colley S., Culkin F. and Sørensen J. (1986) Oxidation fronts in pelagic sediments: diagenetic formation of metal-rich layers. *Science* **232**, 972–975.